

(12) **UK Patent Application** (19) **GB** (11) **2 258 258** (13) **A**

(43) Date of A publication 03.02.1993

(21) Application No 9215569.6

(22) Date of filing 22.07.1992

(30) Priority data

(31) 9116277 (32) 27.07.1991 (33) GB

(71) Applicant

David Brankling
5 Spring Tyne, Westhill, Skene,
Aberdeenshire, AB32 6NH, United Kingdom

(72) Inventor

David Brankling

(74) Agent and/or Address for Service

Murgitroyd & Company
373 Scotland Street,
Glasgow, G5 8QA, United Kingdom

(51) INT CL⁶

C09K 7/06

(52) UK CL (Edition L)

E1F FGP

(56) Documents cited

None

(58) Field of search

UK CL (Edition K) E1F FGP

INT CL⁶ C09K

On-line data base: WPI

(54) **Drilling fluid emulsion composition**

(57) A drilling fluid composition in which the continuous phase of an emulsion comprises a linear alkyl benzene. Preferably the alkyl group has from 4 to 40 carbon atoms.

GB 2 258 258 A

1 "Drilling Fluid"

2

3 This invention relates to drilling fluid for use in the
4 drilling of wells.

5

6 Drilling fluids are circulated down a wellbore during
7 well drilling operations. The fluid is usually pumped
8 down a central drillstring, passes through the drill
9 bit into the wellbore and then returns to the surface.
10 The fluid is then recovered, solid materials extracted,
11 processed and reused.

12

13 Drilling fluids are required to remove rock cuttings
14 generated during the boring process, to lubricate and
15 cool the drill bit and maintain the integrity of the
16 hole. Physical properties of the drilling fluid such
17 as viscosity, density, salinity and filtrate loss may
18 be modified by chemical addition as necessary.

19

20 One major problem which occurs in the use of water
21 based drilling fluids is the hydration of rock being
22 drilled; this is particularly acute when the interval
23 contains clays and shales. These materials exhibit a
24 great affinity for water and adsorption leads to
25 swelling of the rock with resultant stresses leading to

1 collapse of the borehole or loss of structure.

2

3 Such failures lead to wellbore expansion, stuck pipe,
4 excessive rheology, and general drilling problems.

5

6 A second problem with water based drilling fluids which
7 is particularly prevalent in the North Sea is the
8 drilling of so called "salt stringers ". These
9 intervals comprise regions of high concentrations of
10 water soluble salts such as sodium, magnesium and
11 potassium chloride which will dissolve in the drilling
12 fluid and lead to hole enlargement, washout and general
13 failure of the wellbore.

14

15 One solution to the above problems has been the use of
16 so called "salt saturated" solutions in which a soluble
17 salt, usually sodium chloride, is dissolved at maximum
18 concentration in the aqueous medium and used as the
19 drilling fluid base. Such solutions limit shale
20 hydration and prevent further dissolution of drilled
21 salts into the fluid.

22

23 However, salt saturated solutions are expensive, have
24 limitations on the density range which may be used and
25 limit the number of additives which may be used to
26 control the properties of the drilling fluid.

27

28 A second and more widely applied solution involves the
29 use of oil based drilling fluids which are usually
30 formulated with mineral oils. These fluids comprise a
31 salt-containing aqueous phase which is tightly
32 emulsified into an external oil phase by the use of
33 suitable surfactants.

34

35 Oil based drilling fluids therefore present to the

1 surface of drilled rocks an inert oil phase which will
2 not hydrate shale nor dissolve salt. Further, cuttings
3 recovered from oil based fluids are covered with a thin
4 film of oil which prevent hydration and breakage.

5
6 Oil based drilling fluids have a much wider range of
7 density, rheology, thermal stability and application
8 than salt saturated or water based fluids and are
9 widely used.

10
11 However, disposal of rock cuttings which contain a
12 significant proportion of water insoluble oil,
13 especially by disposal through marine dumping at the
14 drill site, is becoming environmentally unacceptable.

15
16 In attempts to upgrade the performance of water based
17 fluids further additives have been used to attempt to
18 control shale hydration, for example potassium
19 chloride, polyacrylamide, polyglycerols, carboxymethyl
20 derivatives, gilsonite, calcium chloride and sodium
21 silicate. However, none of these systems have proved
22 to match the performance of oil based fluids and
23 importantly have minimal effect in preventing solution
24 of salt sections.

25
26 There exists a need for an environmentally acceptable
27 alternative to oil based drilling fluid which exhibits
28 control of both shale hydration and salt dissolution
29 and which may be used over the density range covered by
30 oil based fluids.

31
32 Currently-used oil based drilling fluids are described
33 as "low toxicity" by virtue of the highly refined
34 nature of the base oils which contain only a small
35 percentage of aromatic compounds which can be harmful

1 to marine life or to the product handler. However,
2 such fluids are very poorly degraded and will remain as
3 a persistent contaminant at disposal sites for many
4 years.

5
6 "Low toxicity" oils are produced by a series of
7 fractionation and occasionally solvent
8 extraction/precipitation processes from crude oils and
9 hence contain a broad range of molecular structures
10 only a small number of which are biodegradable.

11
12 However, hydrocarbons having similar structures to
13 mineral oil may be prepared synthetically by
14 polymerisation of ethylene or other unsaturated gases
15 and liquids in manufacturing processes such as the
16 Shell higher olefins process (SHOP). The resultant
17 polyalphaolefins (PAO) are high purity compounds which
18 because of the linear structure are highly
19 biodegradable. Such a property would make a highly
20 desirable alternative fluid to conventional mineral oil
21 based drilling fluids.

22
23 However, another desirable property of the oil
24 component of an oil based drilling fluid is that the
25 oil should have a high flash point to ensure safety in
26 use and a low freezing point to enable liquid handling
27 under the low temperatures experienced during winter
28 use or in low temperature regions of the world.

29
30 The flash point of a polyalphaolefin increases as the
31 molecular weight increases but unfortunately the
32 freezing point also rapidly increases such that liquid
33 handling becomes difficult.

34
35 In addition polyalphaolefins contain a reactive

1 unsaturate terminal grouping which is prone to
2 oxidation, polymerisation and undesirable reactions
3 which can lead to a change in the physical properties
4 of the fluid and could cause problems during the
5 drilling process.

6
7 Other highly refined mineral oils such as liquid
8 paraffins or polyalphaolefins stabilised by
9 hydrogenation to yield liquid paraffins also suffer
10 from the problem of high freezing point in high flash
11 point fractions.

12
13 According to the present invention there is provided
14 drilling fluid comprising an emulsion whose continuous
15 phase comprises a linear alkyl benzene (LAB).

16
17 The LAB is selected to replace the mineral oil content
18 of conventional oil based drilling fluids in which the
19 oil phase may consist of naphthenic, paraffinic and
20 aromatic oils such as diesel, refined base oils, liquid
21 paraffins and polyalphaolefins.

22
23 Linear alkyl benzenes provide a high flash point, low
24 freezing point, stable liquid of good biodegradability
25 which can be advantageously used to replace mineral oil
26 in drilling fluid.

27
28 The resultant drilling fluid may be used to replace
29 conventional "clean oil" drilling muds but is
30 inherently biodegradable and may be treated or disposed
31 of safely to the surrounding environment.

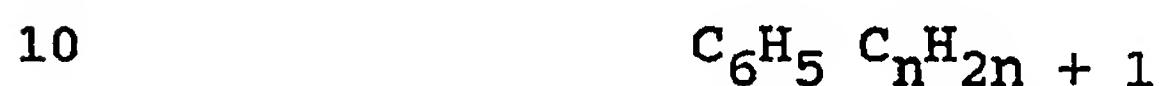
32
33 In addition the replacement of paraffinic "clean oil"
34 by a linear alkyl benzene considerably increases the
35 polarity of the drilling fluid oil phase such that

1 improved surfactant, emulsion and gellant
2 characteristics are obtained from mud additives
3 designed to effect the mud emulsion and convey suitable
4 rheology to the system.

5

6 The structure of the linear alkyl benzene used as the
7 hydrocarbon phase of the drilling fluid emulsion is
8 given by the formula:

9



11

12 where n is an integer from 4 to 40,
13 preferably 4 to 30 and most preferably 4
14 to 20.

15

16 The minimisation of branched alkyl benzene content is
17 necessary to maximise biodegradability of the fluid.

18

19 Suitable compounds may for example be produced by the
20 reaction of chlorinated paraffins or olefins with
21 benzene in the presence of Friedel-Crafts catalyst, or
22 the direct reaction of polyalphaolefin with benzene in
23 the presence of hydrogen fluoride.

24

25 The resultant LAB may then be used as the external
26 phase of an oil based emulsion at preferable oil/water
27 ratios varying from 25/75 to 100/0.

28

29 Additives may be included in the fluid such as fluid
30 loss additives, weighting agents such as barite and
31 haematite, and speciality polymers.

32

33 Gelling agents, viscosity-controlling agents and
34 water-soluble salts may also be present, and
35 hydrocarbon oil and oil-soluble ester may be included

1 in the continuous phase of the emulsion.

2

3 The emulsified water content of the drilling fluid may
4 contain dissolved salts such as sodium chloride,
5 potassium chloride, calcium chloride, potassium acetate
6 or any other soluble material added to adjust the
7 resultant salt solution and drilling fluid density or
8 to change the brine properties to enhance drilling.

9

10 The emulsifion may also contain natural brines such as
11 sea water, aquifier fluids or may be fresh water of
12 minimal dissolved salt content.

13

14 A component of the drilling fluid composition is
15 preferably a surfactant which emulsifies the aqueous
16 phase into the LAB and may typically be an organic
17 acid, amide, ethoxylate, amine, phosphate, propoxylate
18 or combination thereof.

19

20 Embodiments of the invention will be described by way
21 of illustration in the following Examples.

22

23 The flash point of a series of liquid hydrocarbons has
24 been measured by a closed cup technique in conjunction
25 with an observed melting point (freezing temperature)
26 for each material and kinematic viscosity at 40°C.

27

28 Oil type	Flash	Freezing	Viscosity
29	Point/°C	Point/°C	/cSt

30

31 Conventional
32 "clean oils"

33 BP 83HF*	100	-32	2.9
-------------	-----	-----	-----

34 Total HDF 200*	110	-30	3.2
-------------------	-----	-----	-----

35

1	Alpha olefins			
2	(typical)			
3	C ₈	15	-102	0.7**
4	C ₁₄	102	-14	2.75**
5	C ₁₈	150	+17	3.3
6				
7	Linear alkyl			
8	benzene			
9	C ₈ - C ₁₀	123	<-70	3
10	C ₁₀ - C ₁₂	130	<-70	4
11	C ₁₁ - C ₁₃	135	<-70	4
12				

13 *Trade name

14 **Viscosity at 20°C

15

16 The above figures shown that LAB's exhibit very low
 17 freezing points and high flash points exceeding the
 18 performance of conventional "clean oils".

19

20 However, the precursor polyalphaolefins exhibit much
 21 higher freezing points at equivalent flash points which
 22 may cause problems in liquid handling under typical
 23 field conditions.

24

25 Drilling fluid emulsions in which linear alkyl benzene
 26 is used to replace the oil content of a conventional
 27 clean oil system have been prepared according to the
 28 procedure below.

29

30 An invert emulsion mud was prepared by mixing the
 31 following material quantities together on a Silverson
 32 blender at room temperature:

33

34 187.7 ml of hydrocarbon phase

35 12 g Kleemul 50 (emulsifier/surfactant)

1 from BW Mud Ltd)
2 6 g Calcium oxide
3 6 g Emulhivis (treated organoclay
4 viscosifier from BW Mud Ltd)
5 144 ml of a 25% solution of calcium
6 chloride
7
8 Once the drilling fluids had been prepared the mud
9 rheologies and electrical stability were measured at
10 49°C, fluid loss monitored at 121°C and 500 psi
11 differential.
12
13 The prepared fluids were then hot rolled at 121°C for
14 16 hours and mixed properties remeasured.
15
16 Linear alkyl benzenes obtained from Shell Chemicals
17 under the trade names Dobane 83 and Dobane 103 were
18 compared with a conventional "clean oil" from Shell
19 branded as Shellsol DMA.
20
21 The above formulations result in 60/40 oil system of
22 typical North Sea composition.
23
24 COMPARATIVE EXAMPLE 1 using Shellsol DMA
25
26 Apparent viscosity 35 cP
27 Yield point 9.6 Pa (20 lb/100 ft²)
28 Plastic viscosity 25 cP
29 Gel strengths 5.3/5.8 Pa (11/12 lb/100 ft²)
30 Fluid loss 4.0 ml
31 Electrical stability 279 V
32
33 After hot rolling sample:
34
35 Apparent viscosity 36 cP

1	Yield point	11.5 Pa (24 lb/100 ft ²)
2	Plastic viscosity	24 cP
3	Gel strengths	4.8/5.8 (10/12 lb/100 ft ²)
4	Fluid loss	4.0 ml
5	Electrical stability	309 V

6

7 EXAMPLE 1

8

9 A drilling fluid was prepared using Dobane 83 a C₈ -
10 C₁₃ linear alkyl benzene available from Shell Chemicals
11 UK Ltd.

12

13	Apparent viscosity	53.5 cP
14	Yield point	16.8 Pa (35 lb/100 ft ²)
15	Plastic viscosity	36 cP
16	Gel strengths	7.2/6.7 Pa (15/14 lb/100 ft ²)
17	Fluid loss	2.0 ml
18	Electrical stability	166 V

19

20 After hot rolling sample:

21

22	Apparent viscosity	62 cP
23	Yield point	21.1 Pa (44 lb/100ft ²)
24	Plastic viscosity	40 cP
25	Gel strengths	9.1/10.1 Pa (19/21 lb/100 ft ²)
26	Fluid loss	2.2 ml
27	Electrical stability	495 V

28

29 EXAMPLE 2

30

31 A drilling fluid was prepared using Dobane 103 a C₁₀ -
32 C₁₃ linear alkyl benzene available from Shell Chemicals
33 UK Ltd.

34

35	Apparent viscosity	62 cP
----	--------------------	-------

1	Yield point	21.1 Pa (44 lb/100 ft ²)
2	Plastic viscosity	40 cP
3	Gel strengths	9.1/8.6 Pa (19/18 lb/100 ft ²)
4	Fluid loss	2.0 ml
5	Electrical stability	169 V
6		
7	After hot rolling sample:	
8		
9	Apparent viscosity	75 cP
10	Yield point	25.9 Pa (54 lb/100 ft ²)
11	Plastic viscosity	48 cP
12	Gel strengths	12.5/13.4 Pa (26/28 lb/100 ft ²)
13	Fluid loss	2.4 ml
14	Electrical stability	612 V

15

16 COMPARATIVE EXAMPLE 2

17

18 A drilling fluid of 50/50 Shellsol DMA (prior
 19 art)/water ratio was prepared by blending the following
 20 materials on a Silverson emulsifier:

21

22	230 ml	Shellsol DMA
23	19.9 g	Kleemul 50
24	8.3 g	Lime
25	4.95 g	Emulhivis
26	232 ml	Water
27	46.35 g	Calcium chloride

28

29 The resultant emulsion properties were:

30

31	Apparent viscosity	32.5 cP
32	Yield point	6.2 Pa (13 lb/100 ft ²)
33	Plastic viscosity	26 cP
34	Gel strengths	3.4/3.4 Pa (7/7 lb/100 ft ²)
35	Electrical stability	129 V

1

2 It is clear that in comparison with Comparative Example
3 1 the electrical stability value and hence emulsion
4 stability of the drilling fluid is much reduced.

5

6 EXAMPLE 3

7

8 A drilling fluid according to the formulation given in
9 Comparative Example 2 was produced using Dobane 83 in
10 place of Shellsol DMA.

11

12 The resultant emulsion properties were:

13

14	Apparent viscosity (49°C)	65 cP
15	Yield point	21.1 Pa (44 lb/100 ft ²)
16	Plastic viscosity	43 cP
17	Gel strengths	8.6/8.6 Pa (18/18 lb/100 ft ²)
18	Electrical stability	192 V

19

20 A comparison of the properties of this 50/50 emulsion
21 drilling fluid with the fluid produced in Example 1 at
22 a 60/40 ratio demonstrates no loss in electrical
23 stability. That is, the linear alkyl benzene results
24 in a high stability emulsion although the water content
25 has increased.

26

27 EXAMPLE 4

28

29 A drilling fluid according to the formulation in
30 Comparative Example 2 was produced using Dobane 103 in
31 place of Shellsol DMA.

32

33 The resultant emulsion properties were:

34

35 Apparent viscosity (120°F) 75.5 cP

1	Yield point	24.5 Pa (51 lb/100 ft ²)
2	Plastic viscosity	50 cP
3	Gel strengths	10.1/11.5 Pa (21/24 lb/100 ft ²)
4	Electrical stability	153 V

5
6 In comparison with Example 2 using a higher 60/40
7 oil/water ratio the 50/50 emulsion produced shows an
8 emulsion electrical stability of similar value, that is
9 of enhanced performance compared to the prior art clean
10 oil system of Comparative Example 2.

11
12 Linear alkyl benzene therefore demonstrates improved
13 stability in high water content drilling fluids and
14 produces fluids of satisfactory rheology, fluid loss
15 and thermal stability suitable for drilling operations.

16

17 EXAMPLE 5

18

19 A drilling fluid was prepared using PETRELAB P 400, a
20 linear alkyl benzene of C₁₀ - C₁₂ alkyl side chain
21 produced by Petroquimica Expanola (PETRESA) of Spain
22 and commercially available as a detergent alkylate.

23

24 The formulation was compared against the base oil BP
25 83HF, a conventional clean oil produced by BP
26 Chemicals.

27

28 Fluids were mixed using a laboratory blender to give a
29 50/50 system of the following composition:

30

31	109.1 ml	P 400 or BP 83HF
32	12 g	Kleemul 50 surfactant emulsifier
33	6 g	lime
34	2 g	Perchem DMB organoclay gellant
35		from Akzo Chemicals

1 128.2 ml water
 2 56.2 g calcium chloride (82-85%)
 3 barite to give a density of 1.43
 4 (12 ppg)

5
 6 Each fluid was tested for rheology at 49°C and then hot
 7 rolled at 121°C for 16 hours before remeasuring
 8 properties.

9				
10	Oil Phase	Akyl benzene P 400 Clean Oil BP 83HF		
11		BHR	AHR	BHR AHR
12	Apparent viscosity/cP	92	93	65 79
13	Yield point/Pa	12.5	27.8	10.6 17.3
14	Plastic viscosity/cP	79	64	54 61
15	Gels/Pa	4.8/8.2	4.8/9.1	2.9/4.8 3.8/6.2
16	Electrical stability/V	418	580	460 561
17	Fluid loss at:			
18	500 psi/121°C	-	4.4 ml	- 7.6 ml

19
 20 The use of an alkylbenzene P 400 gives improved
 21 rheology (increased yield point and gel strengths) and
 22 improved fluid loss control.

23
 24
 25
 26
 27
 28
 29
 30
 31
 32
 33
 34
 35

1 Claims

2

3 1 Drilling fluid comprising an emulsion whose
4 continuous phase comprises a linear alkyl benzene.

5

6 2 Drilling fluid according to Claim 1, in which the
7 linear alkyl benzene contains an alkyl group having
8 from 4 to 40 carbon atoms.

9

10 3 Drilling fluid according to Claim 1, in which the
11 linear alkyl benzene contains an alkyl group having
12 from 4 to 30 carbon atoms.

13

14 4 Drilling fluid according to Claim 1, in which the
15 linear alkyl benzene contains an alkyl group having
16 from 4 to 20 carbon atoms.

17

18 5 Drilling fluid according to any one of the
19 preceding Claims, in which the ratio of total
20 linear alkyl benzene to water in the emulsion is
21 from 25/75 to 100/0 by volume.

22

23 6 Drilling fluid according to any one of the
24 preceding Claims, containing also a surface active
25 agent.

26

27 7 Drilling fluid according to any one of the
28 preceding Claims, containing also a gelling agent.

29

30 8 Drilling fluid according to Claim 7, in which the
31 gelling agent is selected from clay, modified
32 organoclays, polymers and resins.

33

34 9 Drilling fluid according to any one of the
35 preceding Claims, containing also a weighting

1 agent.

2

3 10 Drilling fluid according to Claim 9 , wherein the
4 weighting agent is barite.

5

6 11 Drilling fluid according to any one of the
7 preceding claims, containing also a water-soluble
8 salt.

9

10 12 Drilling fluid according to any one of the
11 preceding claims, containing also a material which
12 controls fluid loss.

13

14 13 Drilling fluid according to any one of the
15 preceding claims, containing also a
16 viscosity-controlling agent.

17

18 14 Drilling fluid according to any one of the
19 preceding claims, containing also a hydrocarbon oil
20 in the continuous phase of the emulsion.

21

22 15 Drilling fluid according to any one of the
23 preceding Claims, containing also an oil-soluble
24 ester in the continuous phase of the emulsion.

25

26 16 Drilling fluid substantially as hereinbefore
27 described with reference to any one of Examples 1
28 to 5.

29

30

31

32

33

34

35

Patents Act 1977

**Examiner's report to the Comptroller under
Section 17 (The Search Report)**

Application number

GB 9215569.6

Relevant Technical fields

(i) UK CI (Edition K) E1F (FGP)

(ii) Int CI (Edition 5) C09K

Search Examiner

D B PEPPER

Databases (see over)

(i) UK Patent Office

(ii) ONLINE DATABASE: WPI

Date of Search

25 AUGUST 1992

Documents considered relevant following a search in respect of claims

1-16

Category (see over)	Identity of document and relevant passages	Relevant to claim(s)
	NONE	

SF2(p)

Category	Identity of document and relevant passages	Relevance to claim(s)

Categories of documents

X: Document indicating lack of novelty or of inventive step.

Y: Document indicating lack of inventive step if combined with one or more other documents of the same category.

A: Document indicating technological background and/or state of the art.

P: Document published on or after the declared priority date but before the filing date of the present application.

E: Patent document published on or after, but with priority date earlier than, the filing date of the present application.

&: Member of the same patent family, corresponding document.

Databases: The UK Patent Office database comprises classified collections of GB, EP, WO and US patent specifications as outlined periodically in the Official Journal (Patents). The on-line databases considered for search are also listed periodically in the Official Journal (Patents).